

Consensus-Based Sediment Quality Guidelines

Recommendations for Use & Application

Interim Guidance

Developed by the Contaminated Sediment Standing Team

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GOVERNOR

Jim Doyle

NATURAL RESOURCES BOARD

Trygve Solberg, Chair
James Tiefenthaler Jr., Vice Chair
Gerald O'Brien, Secretary
Herbert F. Behnke
Howard D. Poulson
Jonathan P. Ela
Stephen D. Willett

Wisconsin Department of Natural Resources

Box 7921 Madison, WI 53707

Scott Hassett, Secretary William H. Smith, Deputy Secretary Elizabeth Kluesner, Executive Assistant

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The Contaminated Sediment Standing Team is sponsored by:

Bureau of Remediation and Redevelopment, Air and Waste Division

Bureau of Watershed Management, Water Division

Contaminated Sediment Standing Team Members:

Tom Aartilla	Jim Hosch	Liesa Niesta
Jim Amrhein	Tom Janisch	Kelly O'Connor
Margaret Brunette	Jim Killian	Jennie Pelczar
Bill Fitzpatrick	Ed Lynch	Candy Schrank
Steve Galarneau	Paul Luebke	Linda Talbot
Bob Grefe	Al Nass	Xiaochun Zhang

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Consensus - Based Sediment Quality Guidelines; Recommendations for Use & Application

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Consensus - Based Sediment Quality Guidelines; Recommendations for Use & Application

1. Overview

- Wisconsin DNR needs effects-based (i.e., empirical) sediment quality guidelines (SQGs) for commonly found, in place contaminants to serve as benchmark values for making comparisons to the concentrations of contaminant levels in sediments at sites under evaluation for various reasons (e.g., NR 347 dredging projects, degree and extent studies, screening level ecological risk assessments). There is a need for these values on lower assessment tiers and on a screening level basis and for other objectives during different phases of a site assessment.
- In the last few years, a number of entities have generated effects-based SQGs for some of the
 more widely measured contaminant metal and organic chemical compounds. Most of the
 guidelines have focused on effects to benthic-dwelling species. Watershed program staff have
 used some of the guidelines for evaluating sediment quality at initial or lower tiers in the
 assessment process for the sediment quality at sites.
- The most recent development in sediment quality guidelines is where the effect-level concentrations from several guidelines of similar narrative intent are combined through averaging to yield consensus-based lower and upper effect values for contaminants of concern (e.g., MacDonald *et al.* 2000a). The consensus-based values have been evaluated for their reliability in predicting toxicity in sediments by using matching sediment chemistry and toxicity data from field studies. The results of the reliability evaluation showed that most of the consensus-based values for individual contaminants provide an accurate basis for predicting the presence or absence of toxicity (MacDonald *et al.* 2000a). To predict the toxicity for mixtures of various contaminants in sediments, the concentration of each contaminant is divided by its corresponding probable effect concentration (PEC). The resulting values are called PEC-Quotients (PEC-Q). The individual PEC-Qs are summed and divided by the number of PEC-Qs to yield a mean PEC-Q. Using relationships derived from existing databases, the mean PEC-Q value can be used to predict the toxicity of a mixture of contaminants in a sediment sample. The appendix provides further explanation and examples of calculating and combining PEC-Q values.
- The CBSQGs as developed only involve effects to benthic macroinvertebrate species. A large amount of databases from toxicological research have established the cause and effect or correlations of sediment contaminants to benthic organism and benthic community assessment endpoints. The guidelines do not consider the potential for bioaccumulation in aquatic organisms and subsequent food chain transfers and effects to humans or wildlife that consume the upper food chain organisms. For the most part where noncarcinogenic or nonbioaccumulative organic chemicals are involved, the guidelines should be protective of human health and wildlife concerns. Where bioaccumulative compounds such as PCBs and methyl mercury are involved, protection of human health or wildlife-based endpoints could result in more restrictive sediment concentrations than contained in the CBSQGs. Where these bioaccumulative compounds are involved, the CBSQGs need to be used in conjunction with other tools, such as human health and ecological risk assessments, bioaccumulation-based guidelines, bioaccumulation studies, and

tissue residue guidelines to evaluate the direct toxicity and upper food chain effects of these compounds. Food chain models will need to be used to estimate safe levels of contaminants in sediments that will not result in accumulated levels in upper food chain organisms that exceed toxicity and tissue reference values.

- There are a number of program needs and uses for sediment quality guidelines during a tiered assessment process for a site under investigation related to further investigative and management decisions. For consistency sake, we recommend that the consensus-based SQGs (CBSQGs) as currently developed by MacDonald et al. (2000a) be utilized in appropriate situations by all Department programs for screening sediment quality data to help estimate the likelihood of toxicity, as staff evaluate the available information in order to make case-by-case investigative and management decisions for a site. For chemicals for which CBSQGs are not available, we recommend utilizing the most reliable of other effects-based freshwater SQGs that have been published in the scientific literature or developed by WDNR or other regulatory entities. In the SQG tables that follow, these latter values are included and identified as to source. In most cases, the guidelines will need to be backed by additional sampling and field studies at sites under investigation to support the guideline-predicted biological effects.
- The MacDonald et al. (2000a) CBSQGs have a lower (threshold effect concentration TEC) and upper (probable effect concentration PEC) effect level at which toxicity to benthic-dwelling organisms are predicted to be unlikely and probable, respectively. There is an incremental increase in toxicity as the contaminant concentrations increase between the TEC and PEC concentrations, although specific numerical values relating to the degree of toxicity can't be derived. Based on the ranges of concentration related to the TEC and PEC values, we have developed a qualitative descriptor system to be used to provide a common basis of expressing relative levels of concern with increasing contaminant concentrations. The resulting levels of concern can be used to rank and prioritize sites for additional investigation phases. The midpoint effect concentration (MEC) is a concentration midway between the TEC and PEC concentrations.

Level of Concern	Threshold Effect Concentration (TEC)	Level of Concern	Midpoint Effect Concentration (MEC)	Level of Concern	Probable Effect Concentration (PEC)	Level of Concern
Level 1	From	Level 2	TEC + PEC / 2	Level 3	From	Level 4
≤ TEC	CBSQGs	> TEC ≤ MEC	= MEC	> MEC ≤ PEC	CBSQGs	> PEC

• Development of sediment quality guidelines is an evolving science. As additional SQGs with applicability to Wisconsin sites and reliability in predicting toxicity are developed, they in turn should be evaluated for possible replacement of the CBSQGs as appropriate. There is a need to continually reexamine the appropriate use of SQGs as management tools and to refine uses of SQGs to better predict toxicity and/or biological community impairment (Fairey et al. 2001). Given the 1) variable environmental and site-specific factors that control the sequestering, release, and bioavailability of contaminants in sediments, 2) the effects of varying mixtures of sediment contaminants, and 3) the variable sensitivities and exposure and uptake routes of benthic macroinvertebrates to contaminants, there is a continued need for guidelines to be supported by site-specific field studies. Along with numerical guidelines, biological criteria based on specific toxicity tests and identified endpoints (e.g., mortality, growth, and reproduction to the test organisms) and benthic community study metrics should be established and used, as

appropriate, in evaluating sediment quality. Levels of acceptable reductions in the endpoints (e.g., no more than 20% reduction [p < 0.05] in endpoint response compared to the reference site or control site results in toxicity tests) that can be extrapolated to have ecological relevance for the survival of populations in the field should be established (Lawrence, 1999; Michelsen, 1999; Chapman *et al.* 1997; Suter, 1996; and Suter and Tsao, 1996) and used in the evaluation and management decisions for a contaminated sediment site.

2. Introduction

Over the past several years, different entities including several states, Canadian provinces, U.S. EPA, and various researchers have each developed sets of effects-based SQGs. The guidelines were generally developed using empirical approaches that established databases that related a range of effects (e.g. reduced survival, growth, or reproduction of benthic macroinvertebrate organisms) to a range of increasing concentrations of individual sediment-associated contaminants. The guidelines generally established two concentration levels based on effects - a lower effect level at which no or minimal effects are predicted and an upper effect concentration level at which adverse effects are highly probable or will frequently be seen. The focus for all the sets of guidelines was primarily on developing concentrations that would be protective of the majority of bottom dwelling species that reside on or in the sediments and sediment pore water. The developed guidelines generally do not consider the food chain aspects of such bioaccumulative compounds as methyl mercury and the nonpolar organic compounds (e.g., PCBs) in terms of effects to humans or wildlife.

During the early-1990's, the sediment staff within the Water Quality Standards Section of the Bureau of Watershed Management had initially used effects-based guidelines developed by the province of Ontario in Canada (Persaud *et al.*1993) and NOAA (1991) in doing screening level assessments of sediment quality for various sediment projects (e.g., NR 347 assessments and in relationship to site investigations conducted at a number of sites). In 1996, based on the studies of contaminated sediments in the Great Lakes, U.S. EPA (Ingersoll *et al.* 1996a, 1996b) produced a set of sediment quality guidelines that Water Program staff incorporated into doing assessments along with the above two sets of guidelines. The Ontario and U.S. EPA guidelines are relevant because they were developed based on databases from studies involving benthic macroinvertebrate species and sites from the Great Lakes region. Since the U.S. EPA guidelines were published, several other sets of guidelines have been developed and published (MacDonald and MacFarlane, 1999 and CCME, 1999).

The most recent development in SQGs is the consensus-based SQGs (CBSQGs) in which the geometric mean of several sets of SQGs of similar narrative intent have been integrated to yield "consensus based" lower (threshold effect concentration - TEC) and upper (probable effect concentration - PEC) effect levels (MacDonald *et al.* 2000a, 2000b; Swartz, 1999). The CBSQGs of MacDonald *et al.* (2000a) have been adopted for use as sediment quality targets in the St. Louis River Area of concern (Crane *et al.* 2000). Prior to publication of the above consensus-based guidelines in the literature, Water Program staff used the consensus-based approach to develop sediment quality guidelines for a number of metals based on averaging the effect levels from several sets of guidelines. The latter sediment quality objectives are now being superceded by our recommendation that the CBSQGs of MacDonald et al. (2000a) be used for all future sediment quality assessments.

3. Recommendations On the Type of Sediment Quality Guidelines To Be Used

For the sake of consistency on a statewide basis in doing initial screenings of sediment quality in the lower tiers of a site assessment and for other uses, it is recommended that:

- 1) The CBSQGs as developed by MacDonald et al. (2000a) for the protection of benthic organisms should be considered for use by all evaluators;
- Reliable effect-based freshwater sediment quality guidelines published in the scientific literature or in Water Quality Standards Section development memos should be used for contaminants for which CBSQGs are not available; and
- 3) Because points 1 and 2 above principally involve protective levels for benthic organisms, other approaches such as food chain modeling and back calculating from acceptable fish tissue levels should be used to establish protective levels of bioaccumulative contaminants in sediments for ecological receptors and humans. Water Quality Standards Section staff tentatively plan to develop a separate technical paper that lists the approaches available and calculation methods of each approach to derive concentrations of contaminants in sediments that would be protective of humans and ecological receptors such as birds and wildlife.

4. The Uses of Sediment Quality Guidelines

As discussed above, there is a need for effects-based sediment SQGs for commonly found contaminants in order to compare to the concentrations that may be in the sediments of a site under study. There is a need for these values on a screening level basis and for other needs during different phases of a site assessment. The uses for CBSQGs include:

- 1) To assess the quality of prospective dredged materials (NR 347 dredging projects) related to potential effects both in place, during removal activities, and at the completion of removal activities. The possible impacts of residual contaminant levels left exposed at the project depth and/or in the side walls at the project boundaries also need to be evaluated.
- 2) To screen study site contaminant concentrations to evaluate the relative degree of potential risks and impacts to sediment dwelling species.
- 3) To identify and to help prioritize sites for additional studies based on the relative degree and extent of contamination, size of contaminated deposits, and potential risks to benthic receptors. These steps can allow for a systematic basis for prioritorizing sites for allocation of available funding and resources for further monitoring.
- 4) To evaluate the need to collect additional sediment chemistry data, based on initial screening results, and determine the need to do a concurrent collection of biological data (e.g., toxicity testing and macroinvertebrate community studies) in a second study phase to more adequately characterize the degree and extent of contamination. The biological studies would attempt to validate if the CBSQGs are accurate predictors of toxicity and impacts to the benthic community related to the contaminant concentrations found at a site.
- 5) As toxicity benchmarks in the staged processes associated with screening level ecological risk assessments and the problem formulation stage of baseline ecological risk assessments (Crane *et al.* 2000; Ingersoll *et al.* 1997; U.S. EPA, 1997; WDNR, 1992). Use of the CBSQGs

- as benchmarks for toxicity screening serves to 1) estimate the likelihood that a particular ecological risk exists, 2) helps identify the need for site-specific data collection efforts, and 3) helps to focus site-specific baseline ecological risk assessments.
- 6) As one line of evidence where multiple lines of evidence are used to support decision-making activities for a site in a weight-of-evidence approach. No single line of evidence would be used to drive decision-making. Each line of evidence should be evaluated for the 1) adequacy and quality of the data, 2) degree and type of uncertainty associated with the evidence, and 3) relationship of the evidence to the potential degree of impact being estimated. All of the lines of evidence will be integrated to characterize risk based on: 1) concurrence of all line of evidence results 2) preponderance, 3) magnitude, 4) extent, and 5) strength of relationships between the exposure and the effects data.
- 7) The process for assessing sediment quality as it relates to identifying surface water issues will be based on the tiered assessment framework established by the Department's Contaminated Sediment Standing Team (WDNR, 2001). The tiered framework utilizes numerical CBSQGs in the lower tiers and moves to more comprehensive, structured risk-based assessments in the higher tiers. The diversity of different types of sediment assessments and objectives calls for the need for a flexible framework with options for assessing sediment quality. More information is developed in successive tiers until it can be determined that enough information is available to adequately assess the sediment quality related to biological effects. Reasons for conducting risk-based studies at higher assessment tiers may include 1) the complexity of the interactions of the aquatic ecosystem and the contaminant stressors, 2) diverse mixtures of contaminants may be present at a site, 3) outstanding exposure issues where a risk assessment will allow realistic use of information about the natural history of a species such as foraging areas, breeding times, and migration patterns (Moore et al. 1998), and/or 4) there are unresolved issues with regard to potential human or ecological exposures. A formal risk assessment is not something that needs to be conducted at every sediment site under assessment. The appropriate risk-based studies may need to be designed and carried out at higher assessment tiers. As needed, site-specific studies can progress to effects-based testing and risk-based studies of various designs and scope. Guidance for carrying out such risk-based studies are contained in WDNR guidance documents (1992a; 1992b) and a number of U.S. EPA guidance documents (e.g. U.S. EPA, 1998).
- 8) The CBSQGs should not be used on a stand-alone basis to establish cleanup levels or for sediment management decision making. However, in certain situations, with the agreement of all parties involved in overseeing remediation and those responsible for remediating a contaminated sediment site, the CBSQG values deemed to be protective of the site receptors can be used as the remediation objective for a site (at or approaching the lower effect or threshold effect levels for the contaminant of concern). An example of the latter application was at Gruber's Grove Bay on the Wisconsin River, which was contaminated by discharges containing metals from the Badger Army Ammunition Plant. The Army agreed to clean up the sediments based on the greater of the CBSQG TEC for mercury or the background concentration, in lieu of doing any additional biological assessments or studies for the site. Since the background concentration for mercury was found to be greater than the TEC value, background was used as the remediation objective. Using CBSQGs to drive cleanup of some sites may be preferable under certain conditions (based on considerations of size of site and defined boundaries of contamination) rather than spending a large amount of time and

resources for additional studies and risk assessments that may lead to considerable costs with little benefit. At larger, more complex sites, the costs associated with detailed studies may be warranted to reduce uncertainties and focus resources on the remedial actions that provide the greatest benefits (MacDonald et al. 1999).

9) It should be noted that there may be contaminated sediment sites and situations where a numerical chemical concentration related to effects may not be the primary driver in a sediment cleanup. Based on a number of balancing factors (e.g., technical feasibility of remediation methods, considerations of natural attenuation factors specific to the site, remedial implementability, human health and ecological risks, stakeholder input, and costs) performance-based standards based on the removal of an established mass of contaminant or removal of visual contamination (applicable to coal tars and petroleum oils) from a site may be the remediation action objective rather than a numerical concentration. There may be situations where the above balancing factors will also be considered to derive a factored cleanup concentration that will not initially achieve the science-based protective sediment concentration but may after an established time period (e.g., when factors such as natural attenuation are considered).

5. Considerations and Advantages of Using Consensus-Based Sediment Quality Guidelines

Given the number of guidelines available, selection of any one as the most appropriate and most reliable for ability to predict toxicity and impacts to benthic species at a study site is difficult. Each guideline set was generally developed using a different methodology (e.g. Ontario [Persaud et al. 1993] used the screening level concentration approach and Ingersoll et al.[1996a] used the effect level approach). Each approach for developing guidelines has inherent advantages, limitations, levels of acceptance, different extent of field validation, and differing degree of environmental applicability (EPA, 1992). Selecting one set of guidelines is further complicated by uncertainties regarding the bioavailability of contaminants in sediments, the effects of co-varying chemicals and chemical mixtures, the ecological relevance of the guidelines, and correlative versus causal relations between chemistry and biological effects (MacDonald et al. 2000a). Given these problems, much discussion has taken place over the use of guidelines as a tool for use in doing sediment quality assessments (Peddicord et al. 1998). Cautions are often placed on the use of any one set of quidelines as stand alone decision tools in the assessment and remediation decision making process without additional supporting data from toxicity testing and in-field studies. However, recent evaluations based on combining several sets of guidelines into one to yield "consensus-based" guidelines have shown that such guidelines can substantially increase the reliability, predictive ability, and level of confidence in using and applying the guidelines (Crane et al. 2000; MacDonald et al. 2000 a, 2000 b; Ingersoll et al. 2000). The agreement of guidelines derived from a variety of theoretical and empirical approaches helps to establish the validity of the consensus-based values. Use of values from multiple guidelines that are similar for a contaminant provides a weight-ofevidence for relating to actual biological effects.

A series of papers were produced (Swartz, 1999; Macdonald *et al.* 2000a, 2000b;) that addressed some of the difficulties associated with the assessment of sediment quality conditions using various numerical sediment quality guidelines. The results of these investigations demonstrated that combining and integrating the effect levels from several sets of guidelines to result in consensus-based sediment quality guidelines provide a unifying synthesis of the existing guidelines, reflect causal rather than correlative effects, and can account for the effects of contaminant mixtures in

sediment (Swartz, 1999). Additionally, MacDonald et al. (2000a) have evaluated the consensus-based effect levels for reliability in predicting toxicity in sediments by using matching sediment chemistry and toxicity data from field studies conducted throughout the United States. The results of their evaluation showed that most of the consensus-based threshold effect concentrations (TEC - lower effect level) and probable effect concentrations (PEC - upper effect level) for individual contaminants provide an accurate basis for predicting the absence or presence, respectively, of sediment toxicity.

Ingersoll *et al.* (2000, 2001), MacDonald *et al.* (2000a), and Fairey *et al.* (2001) evaluated the reliability of using mean quotient concentration-related values to predict the toxicity in sediments of a mixture of different contaminants. For example, mean PEC quotients were calculated to evaluate the combined effects of multiple contaminants in sediments (Ingersoll et al. 2000, 2001; MacDonald et al. 2000a). A PEC quotient is calculated for each contaminant in each sample by dividing the concentration of a contaminant in sediment by the PEC concentration for that chemical. A mean quotient was calculated for each sample by summing the individual quotient for each contaminant and then dividing this sum by the number of PECs evaluated. Dividing by the number of PEC quotients normalizes the value to provide comparable indices of contamination among samples for which different numbers of contaminants were analyzed. Results of the evaluation showed that the mean PEC quotients that represent mixtures of contaminants were highly correlated to the incidences of toxicity in the same sediments. See Appendix A for calculation methods and ranges of PEC quotient values that are potentially associated with toxicity.

Based on MacDonald *et al.* (2000a), the consensus-based SQGs can be used for or considered for the following:

- To provide a reliable basis for assessing sediment quality conditions in freshwater ecosystems.
- To identify hot spots with respect to sediment contamination.
- To determine the potential for and spatial extent of injury to sediment-dwelling organisms.
- To evaluate the need for sediment remediation.
- To support the development of monitoring programs to further assess the extent of contamination and the effects of contaminated sediment on sediment-dwelling organisms.

The above applications are strengthened when the consensus-based values are used in combination with other sediment quality assessment tools including effects-based testing (i.e., sediment toxicity tests, bioaccumulation assessments, benthic invertebrate community assessments, and more comprehensive designed risk-based studies).

The consensus-based SQGs as developed only involve effects to benthic macroinvertebrate species. The guidelines do not consider the potential for bioaccumulation in aquatic organisms and subsequent food chain transfers to humans or wildlife. Where bioaccumulative compounds are involved, the consensus-based SQGs need to be used in conjunction with other tools, such as bioaccumulation-based guidelines, bioaccumulation studies, food chain modeling, and tissue residue guidelines to evaluate the direct toxicity and upper food chain effects of these compounds.

The MacDonald et al. (2000a) consensus-based sediment quality guidelines have been adopted by the Minnesota Pollution Control Agency (Crane *et al.* 2000) for use as sediment quality targets in the St. Louis River Area of Concern (AOC) on Lake Superior. Following the recommendation in this guidance for the use of the MacDonald *et al.* (2000a) consensus-based SQGs, which would involve their use on the Wisconsin side of the AOC, would be somewhat consistent with their planned use by Minnesota for making assessment and management decisions for contaminated sediment sites on the Duluth side of the AOC.

6. Interpreting Sediment Concentrations That Fall Between the Lower TEC and Upper PEC Consensus-Based Effect Guideline Concentrations

The greatest certainty in predicting the absence or presence of sediment toxicity occurs at sediment contaminant concentrations that are lower than the TEC or greater than the PEC values, respectively. The development of consensus-based SQGs does not include determining the predictability of toxicity related to specific contaminant concentrations in the gradient between the TEC and PEC values. Generally, a consensus-based value for a contaminant cannot be set within the range between the TEC and PEC that would have a low frequency of both false negatives and false positives (Swartz, 1999). Toxicity does occur at contaminant concentrations between the TEC and PEC values with the amount of toxicity dependent on the particular contaminant and with the incidence of toxicity greater than that which occurs at the TEC concentration but less than that which occurs at the PEC concentration (MacDonald et al. 2000a). The TEC and PEC concentrations in the consensus-based SQGs define three ranges of concentrations for each contaminant (i.e. < TEC; > TEC but < PEC; and > PEC. In assessing the degree of concordance that exists between the chemical concentrations in the three ranges and the incidence of toxicity, it has been demonstrated that for most reliable consensus-based SQG contaminants, there is a consistent and incremental increase in the incidence of toxicity to sediment-dwelling organisms with increasing chemical concentrations (MacDonald et al. 2000a, 2000b).

The databases for some individual sets of guidelines, such as the Ontario guidelines (Persaud et al. 1993) that have been combined with other guidelines to produce the consensus-based SQGs can be interpolated to yield predictions of the percent of benthic species that may be affected at specific concentrations between the lower and upper effect levels. A somewhat conservative but still realistic interpretation that can be applied to contaminant concentrations that fall in the gradient of concentrations between the consensus-based TEC and PEC concentrations is that as the concentrations of a contaminant increase, toxicity and effects to benthic macroinvertebrate species related to reductions in survival, reproduction, and growth, bioaccumulation, and benthic community alterations correspondingly increase and/or are increasingly more probable. An identified limitation of this relationship is that the threshold and nature of this trend can be controlled by factors in specific sediments due to their characteristics (Peddicord *et al.*1998). Site specific effects-based testing can be performed to determine the reliability of the prediction of adverse effects based on the use of the CBSQGs on the lower tiers of the assessment.

It is recommended that for the purposes of interpreting the potential impacts of concentrations of contaminants between the TEC and PEC values of the CBSQGs or other guidelines, that a midpoint effect concentration (MEC) be derived and qualitative descriptors be applied to the four possible ranges of concentration that will be created. The qualitative descriptors would be termed "Concern Levels" and would be used as a relative gauge of the potential impacts to the benthic species at that level of contaminant and could be used to prioritize sites for additional studies. A prioritization scheme

for ranking sites will, in most cases, depend on professional judgment of staff given the fact that sampling data for sites will generally be variable for the number of samples and the number of parameters analyzed for. The descriptive "Concern Level" scheme is shown in the following table for arsenic concentrations and is applied below in Tables 1 – 4 of the CBSQGs for the various grouped contaminants.

Level of Concern	Threshold Effect Concentration (TEC)	Level of Concern	Midpoint Effect Concentration (MEC)	Level of Concern	Probable Effect Concentration (PEC)	Level of Concern			
Level 1	CBSQG	Level 2	TEC + PEC / 2	Level 3	CBSQG	Level 4			
≤ TEC	Value	> TEC ≤ MEC	= MEC	> MEC ≤ PEC	Value	> PEC			
	Example For CBSQG Values for Arsenic (mg/kg)								
≤ 9.8	9.8	> 9.8 ≤ 21.4	21.4	> 21.4 ≤ 33	33	> 33			

7. Recommended Guidelines and Values to be Used in Sediment Quality Assessments

The consensus-based SQG parameters and related effect concentrations in the tables below are from MacDonald *et al.* (2000a) and are indicated in the source column as CBSQGs. Effect-based sediment quality guideline values for some contaminants from other published sources for which CBSQGs were not available are also included in the following tables and identified as such in the source column. These values also represent useful tools for assessing sediment quality. However, their ability to predict toxicity and reliability may not be as great as that for the CBSQGs for a number of reasons including incomplete validation from field testing. This uncertainty has to be weighed in using the values in the assessment process. In cases where more than one set of guidelines have effect-based concentrations for contaminants for which CBSQGs are not available, the effect-based values from that set of guidelines that were the lowest were generally used in the guideline tables that follow. The narrative terminology for effect levels for the latter guidelines may be different from the TEC and PEC terminology from the CBSQGs but the narrative intent is generally the same in establishing a lower and a higher effect level. Also, the emphasis is on those guidelines developed from studies done in freshwater rather than marine or estuarine habitats.

The individual sets of guidelines that were combined and integrated by MacDonald *et al.* (2000a) to yield the CBSQGs are as follows:

Type of SQG	Acronym	Approach	Reference
Derivation of Thresho	old Effect Concentration	on (TEC) CBSQG by MacDonald et al. (2000a) f	rom the following
Lowest Effect Level	LEL	Screening Level Concentration Approach	Persaud <i>et a</i> l. 1993
Threshold Effect Level	TEL	Effect Level Approach	Smith <i>et al.</i> 1996.
Effect Range - Low	ERL	Effect Level Approach	Long and Morgan, 1991
Threshold Effect Level for Hyalella azteca in 28-day tests	TEL-HA28	Effect Level Approach	Ingersoll <i>et al.</i> 1996a and 1996b
Minimal Effect Threshold	MET	Screening Level Concentration Approach	EC and MENVIQ, 1992
Chronic Equilibrium Partitioning Threshold	SQAL (Sediment Quality Advisory Level)	Equilibrium Partitioning Approach	Bolton <i>et al.</i> (1985); Zarba, (1992); U.S. EPA, 1997
Derivation of Probab	le Effect Concentration	n (PEC) CBSQG by MacDonald et al. (2000a) fr	om the following
Severe Effect level	SEL	Screening Level Concentration Approach	Persaud et al. 1993
Probable Effect level	PEL	Effect Level Approach	Smith <i>et al.</i> 1996.
Effect Range - Median	ERM	Effect Level Approach	Long and Morgan, 1991
Probable Effect Level for Hyalella azteca in 28-day tests	PEL-HA28	Effect Level Approach	Ingersoll <i>et al.</i> 1996a and 1996b
Toxic Effect Threshold	TET	Effect Level Approach	EC and MENVIQ, 1992
Acute Equilibrium Partitioning Threshold	No guideline developed		

8. Additional Considerations For Some Contaminants

PAHs

Some sources of the parent or unsubstituted PAHs that are in Table 2, such as creosote, coal tars, and petroleum oils, can have co-occurring compounds such as substituted PAHs and heterocyclic aromatic compounds (carbozoles, indoles, acridines, and quinolines) that can be equally or more toxic and more soluble than the listed parent PAH compounds.

Additionally, photoactivation of certain unsubstituted and substituted PAHs, which enhances their toxicity to aquatic organisms that have bioaccumulated these compounds, has been demonstrated both in the laboratory and in the field. The latter may have implications in certain types of habitats (Ankley et al. 2002).

The possible presence of co-occurring toxic compounds where petroleum oils and coal tars are involved and photoactivation of PAHs at sites may need to be considered or toxicity may be underestimated by looking only at the sediment guidelines for the listed parent PAHs in Table 2.

Dioxins and Furans

Polychlorinated dibenzo dioxins (PCDDs) and Polychlorinated dibenzo furans (PCDFs) are unwanted by products of various chemical manufacturing and combustion processes. They are generally ubiquitous in soils and sediments in urban and rural areas. The potential for greatest levels to be found in environmental media are where chlorinated organic compounds such as certain pesticides and pentachlorophenol were either manufactured or used. Pentachlorophenol use at wood treatment operations (railroad ties, utility poles, or lumber) at some sites in Wisconsin sites has led to dioxin and furan compound contamination in floodplain soils and stream sediments. Another source of PCDDs and PCDFs is from the production of paper products from chlorine-bleached wood pulp.

There are 210 polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) which are based on the points of attachment or substitution of chlorine atoms on the aromatic rings. Of these, 17 (7 dioxins and 10 furans) which have chlorine substituted in the 2,3,7,8 positions are thought to pose the greatest risks to receptor organisms. In order to account for the differing toxicities of the 17 2,3,7,8-substituted isomers, each has been given a toxic equivalency factor (TEF) related to the most toxic form, 2,3,7,8-TCDD (TEF = 1.0). In terms of risk assessments, those PCDDs and PCDFs not substituted in the 2,3,7,8 positions can be ignored. The summed concentration of the TEF of each 2,3,7,8-substituted isomer times its concentration equals the toxic equivalent concentration to 2,3,7,8-TCDD or TCDD-EQ concentration. Appendix C provides a table to calculate a summed TCDD-EQ concentration based on the TEF value and reported concentration for each of the 17 2,3,7,8-substituted isomers found in sediments and floodplain soils.

Cyanide

Cyanide as measured and reported as total cyanides in sediments can include hydrogen cyanide (HCN), cyanide ion (CN⁻), simple cyanides, and metallo- and organo-cyanide complexes. HCN and CN⁻ are grouped as free cyanides and are the most toxic forms of cyanide and the forms of concern.

Most complexed cyanides are relatively nontoxic and total cyanide determinations are not very useful measures of either water or sediment quality. Factors that affect the release or dissociation of free cyanides from complexed cyanide forms include pH, redox potential, photodecomposition of the complex and release of free cyanide, relative strength of the metallo- and organo-cyanide complexes, and possible presence of bacteria responsible for degradation of ferrocyanide complexes. In sediments, the cyanide in the free form present in the pore water is more relatable to toxicity to benthic organisms than the total cyanide measured in the solid phase. However, given the above factors, it is difficult to predict or model the dissociation and release of the free toxic forms of cyanide to the pore water from the less toxic total cyanide form associated with and normally measured in the solid phase sediments. A general idea of the concentrations of free cyanide in pore water that would be toxic to benthic invertebrates can be drawn from the acute and chronic toxicity criteria for free cyanides in surface waters classified as supporting Warm Water Sport Fish (NR 105, Wis. Admin. Code) which are 45.8 ug/L and 11.47 ug/L, respectively. Free cyanides as HCN, in general, are not very persistent in the environment due to their volatility, have low adsorption to sediment particles, high water solubility, and inability to substantially bioaccumulate. Where any significant levels of total cyanide are detected in sediments, additional analysis may need to be done to also determine what fractions of the total cyanide are in dissociable forms (amenable to chlorination or weak acid dissociable forms) to give an indication of the potential to release free cyanide with its attendant toxicity...

9. Background or Reference Site Concentration Considerations In Using the Effect-Based SQGs

In designing and collecting sediment samples at any phase of a site assessment, consideration may need to be given to sampling and analyzing for the same potential chemical stressors, biological data, and/or physical data that are being analyzed for within the study site area at a representative background/reference site to be used as benchmarks for comparison purposes. Establishing representative reference sites is critical because if reference sites are not highly similar to the areas under study, misleading or inappropriate conclusions may be drawn when making data comparisons (Apitz et al. 2002). The background/reference site selected needs to have all the characteristics of the study site sediments as close as practical, which includes similar particle size fractions, total organic carbon content, depositional attributes, and relative positioning (e.g., water depth and stream cross section) in the water body as the study site location, but needs to be out of the influence of the study site and the factors responsible for contaminating the study site. Contributions of contaminants (see Appendix E for a discussion of contamination/contaminant and relation to adverse effects) at the reference site can come from two sources: 1) natural sources based on the soils and geological features in the watershed, and 2) anthropogenic sources such as urban runoff. The reference site should be relatively unaffected by anthropogenic inputs. In urban areas, sediment sites outside of the factors that may be influencing the study site may themselves be influenced by ubiquitous urban sources. The sediment quality of reference sites should be reflective of the land uses and land cover of the watershed that the study site is in. Alternatively, suitable background values may be derived through sediment profiles by examining concentrations at depth with the assumption that the lowest concentration at depth represents the pre-industrial or pre-development sediment horizon (Persaud et al. 1993).

It has to be recognized that in diverse geographical and geological areas, the natural levels of metals and ubiquitous source anthropogenic organic compounds will vary. Given this variation, dependence

should be put on site-specific samples for establishing reference site concentrations rather than depending on data compiled from other unrelated sites. In areas and at sites where the background/reference site concentrations are greater than the CBSQG TEC values, the local background/reference site concentrations should be used as the practical lower limit for doing sediment evaluations and making management decisions for additional sediment assessments.

The particle size fractions (for metals) and total organic carbon (TOC) content (for nonpolar organic compounds) of all samples should be used to normalize concentrations in order to do relevant and appropriate site-to-site comparisons of contaminant concentrations.

TOC can have its origin either from organic matter from natural sources such as plant materials deposited on sediments or anthropogenic inputs to aquatic systems. In the latter case, elevated TOC sources in sediments can be from such sources as residual petroleum oils, coal tars, or creosote. The controlling importance of the amount of natural organic matter as a TOC source for determining the fate and bioavailability of organic chemicals, especially nonpolar or neutral compounds, has been established (U.S. EPA, 1993). A chemically-unique partitioning coefficient ($K_{\rm OC}$) for a nonpolar organic compound is used to estimate the pore water concentration based on its partitioning from natural TOC in the sediment. The partitioning coefficient for a compound is assumed to be relatively constant and predictable across various types of natural organic matter. The $K_{\rm OC}$ values for organic compounds can be found in chemical reference books. Nonpolar organic compounds associated with residual oils of anthropogenic origin as a partition media will have different partitioning coefficients compared to natural organic matter (Boyd and Sun, 1990 and Sun and Boyd, 1991) due to the quality of organic carbon. The latter situation may need to be addressed when estimating the bioavailability of nonpolar organic compounds where the TOC is predominantly contributed by some sources of anthropogenic origin.

For metals and particle size, comparing the concentrations of a contaminant in a sample dominated by a fine fraction with one dominated by a sand fraction would be inappropriate and would not yield useful information. Metals and anthropogenic organic compounds will tend to sorb and concentrate in or on finer grained sediments and TOC, respectively.

The intensity of sampling for establishing representative background/reference site concentrations of contaminants should increase at upper tiers in the sediment evaluation process. For example, for comparisons done in the lower tiers of an assessment when initially investigating the site, one to three sediment samples from the reference site, either analyzed individually or composited for one analysis may be appropriate. Where the reference site concentration comparisons may play a more important role in evaluation and management decisions for a site at upper tiers of an assessment, the sampling intensity should generally increase, with at least 10 or more samples taken at the reference site and analyzed individually. Data sets with fewer than 10 samples generally provide for poor estimates of mean concentrations (i.e., there is a large difference between the sample mean and the 95% upper confidence limit). In most cases, a maximum probable background concentration (MPBC) should be calculated for the contaminant(s) derived from the upper 95% confidence level of the mean (EPA, 1992b) after consideration of the distribution of the sample concentrations as showing either a normal or log normal distribution (see Appendix B for example calculations).

Sample results for a metal or organic compound of concern at the background/reference site may be reported out as a censored value i.e. less than a detection level based on the analytical method that meets the data quality objectives established for the sampling and analysis. There are various

methods to handle the censored data to derive values that can be used with the uncensored values in the data set to derive a mean and standard deviation to be used in the calculation of a maximum probable background concentration. Analyses of methods to handle censored data show that, in most cases, sophisticated statistical techniques recommended for estimation problems involving censored data are unnecessary or even inappropriate for statistical comparisons where the number of censored data samples in a data set are generally small. In general, the simple substitution methods work best to maintain power and control type I error rate in statistical comparisons (Clarke, 1995). The simple substitution method includes either 1) substitution of the detection limit as the quantified concentration, or 2) substitution of one-half the detection limit as the quantified concentration. Clarke (1995) recommends steps in selecting the substitution method. At its simplest, substitution method 1) above should generally be used where the number of censored data results are less than 40% of the data set, and method 2) where the censored data is greater than 40%.

9.1 Metals and Silt/Clay Fraction Relationships

There is a strong correlation between decreasing grain size and increasing metal concentrations. Sand-sized material, which is typically low in trace metal concentrations, may serve as a diluent of metal-rich finer grained particles. Larger fractions of sand can hide significant trace metal concentrations and dispersion patterns (Horowitz, 1991). Adjusting for particle grain size effects is important for 1) determining natural background levels of trace elements associated with sediments to serve as a baseline for comparison purposes with other sites, 2) for distinguishing and determining the degree of anthropogenic enrichment, 3) for comparing metal data from site-to-site on a standardized basis, and 4) providing a means for tracing the extent of metal transport and dispersion by eliminating the diluent effects of large particle size contributions.

Two methods are used to address grain size effects. One is to separate out the sand, silt, and clay sized particles from a sample by sieving and analyzing the separate fractions. The other method is to assume that the majority of the metals in a sample are associated with the fine fraction (silt + clay) and then mathematically normalize the metal data to this fraction by dividing the bulk concentration by the fine fraction percentage expressed as a decimal fraction to yield mg of a metal / kg of fines. Particle size analysis of a sediment sample is usually reported as percent sand, silt, and clay fractions. An example of normalizing a bulk sediment concentration for a metal to the fine fraction for a sample with 84 mg/kg of lead and 60% fines (40% silt + 20% clay) is 84 mg Pb/kg ÷ 0.60 kg fines /kg sediment = 140 mg lead / kg of fines. The assumption may not always hold true that all or most of the metals are associated with the fine fraction. Also, when the fine fraction falls below 50% of the total combined fractions, the mathematical normalization may not represent the true metal concentration in the fines (Horowitz, 1991). The normalization to the fine fractions should at a minimum be done at least qualitatively to compare on a relative basis the fine fraction contents between the sediment samples where the metal concentrations are being compared. Besides grain size, other normalizing factors have been used and include iron, aluminum, and total organic carbon (Daskalakis et al. 1995).

It should be noted that for the CBSQGs for the metals, MacDonald et al. (2000a) do not indicate what the relative percentage of the mineral particle size fractions (% sand, silt, and clay) were assumed to be associated with the expressed values. TOC may play some role in the chemical form of the metal and thus its release from the sediments and its bioavailability. TOC may serve as a secondary binding phase of metals with acid volatile sulfates (AVS) serving as the primary binding phase. It is difficult to predict or measure the role of TOC as it relates to metals. For this reason, the study site

bulk sediment metal concentrations need to be directly compared with the CBSQG concentrations in Table 1 without any adjustments for TOC or fine fraction content. The process above for adjusting metal concentrations based on the percent fines is an additional assessment tool for comparing the concentrations between the unimpacted reference site and the study site and between study sites on a fine content-normalized basis and does not play a role in SQG application.

Normalizing contaminant concentrations to the mineral fine content or TOC content is not to be done for assessing toxicity under TSCA or determining hazardous waste characteristics under the Toxicity Characteristic Leaching Procedure (TCLP) test. The sample dry weight bulk concentrations as reported by the analytical laboratory are to be used for comparison with the applicable criteria under these regulations.

9.2 Nonpolar Organic Compound and Total Organic Carbon Relationships

In the case of nonpolar organic compounds such as PAHs, PCBs, dioxins/furans, and chlorinated pesticides, the bulk sediment concentrations can be normalized to the TOC content for site-to-site comparison purposes by dividing the dry weight sediment concentration by the percent TOC in the sediment expressed as a decimal fraction. For example the TOC normalized PCB concentration for a sediment concentration of 7 mg/kg with 3.5% TOC is 200 mg PCB / kg TOC (i.e., 7 mg PCBs/kg ÷ 0.035 kg TOC/kg = 200 mg PCB/kg TOC). Normalization of nonpolar organic compounds to TOC content is valid only if the TOC content in the sediments is greater than 0.2%. At TOC concentrations less than 0.2%, other factors that influence partitioning to the sediment pore waters (e.g., particle size and sorption to nonorganic mineral fractions) become relatively more important (Di Toro *et al.*1991).

MacDonald *et al.* (2000a) indicate that some individual sets of guidelines that were used in their consensus-based approach were originally expressed on an organic carbon-normalized basis. They converted the values in these sets of to dry weight-normalized values at 1% organic carbon to be averaged with the other sets of guideline values to yield the CBSQGs. The final MacDonald *et al.* (2000a) CBSQG values are expressed on a dry weight basis without regard to organic carbon content. It should be noted that the consensus-based SQG values in Tables 2, 3, and 4 below are expressed on an assumed <u>dry weight normalized basis at 1% organic carbon</u>. It has been established that the organic carbon content of sediment is an important factor influencing the movement and bioavailability of nonpolar organic compounds (e.g., PAHs, PCBs, and chlorinated pesticides) between the organic carbon content in bulk sediments and the sediment pore water and overlying surface water. Biological responses of benthic organisms to nonionic organic chemical in sediments are different across sediments when the sediment concentrations are expressed on a dry weight basis, but similar when expressed on an organic carbon normalized basis (ug chemical / g organic carbon basis) (U.S. EPA, 2000).

To appropriately compare the CBSQG dry weight-normalized to 1% TOC values with the dry weight concentrations in the study sediments of variable TOC content, the study sediment contaminant concentrations also need to be converted to a dry weight-normalized to 1% TOC basis. Appendix D provides a spread sheet for calculating dry weight sediment concentrations for nonpolar organic compounds normalized to 1% TOC. The concentrations given are for an example sediment. Appendix D also contains a spreadsheet for calculating the concentrations of metals normalized to the fine fraction in a sediment sample. An Excel spreadsheet is available for doing the calculations.

An example showing the necessity of doing this conversion to a common 1% TOC basis for organic compounds is shown as follows:

- The threshold effect concentration (TEC) for total PAHs (TPAHs) is 1,610 ug/kg at 1% TOC.
- The example site under assessment has a TPAH concentration of 7,300 ug/kg at 5% TOC.
- Comparing the dry weight concentrations between the guideline value and the example site
 concentration without consideration of the TOC content differences would appear to show that
 the study site concentrations are greater than the TEC guideline value (7,300 study site vs.
 1,610 TEC).
- To convert the study site TPAH concentration to a dry weight concentration normalized to 1%, divide the 7,300 ug/kg value by 5 (5% TOC content) = 1,460 ug TPAH/kg at 1% TOC. On the common basis of 1% TOC, the study site TPAH concentration is less than the TEC concentration (1,460 ug/kg study site vs. 1,610 ug/kg TEC).
- In the case above, another approach for converting the concentrations to a common normalized basis is to multiply the TEC concentration by 5 that is the percent TOC of the study site sample. The common basis here are dry weight-normalized concentrations at 5% TOC (7,300 ug/kg study site vs. 8,050 ug/kg TEC).

10. Point of Application of the CBSQGs in the Bed Sediment

The numerical CBSQGs apply to the biologically active zone associated with deposited sediments in flowing (streams and rivers) and static (lakes and ponds) water bodies and wetland soils and sediments. The biologically active zone is inhabited by infaunal organisms including microbes, meiofauna, and macroinvertebrates and other organisms (e.g., egg and larval stage of fish) that spend all or part of their life cycles associated either within (infaunal) or on (epibenthic) the bottom sediments. The community of organisms present will generally depend on the physical and chemical characteristics of the waterbody and bottom sediments as determined by the watershed location and ecoregion within the State. The depth of the biologically-active zone varies between sites depending on the substrate characteristics present (including particle size fractions, organic matter content, compaction, pore-water geochemistry, and water content) which influence the composition of sediment-associated organisms present. The biologically active zone typically encompasses the top 20 to 40 cm. of sediment in freshwater environments (Clarke et al. 2001). The majority of benthic organisms will usually be associated with the upper strata (e.g., 15 cm) related to these depth ranges. Certain invertebrate and/or amphibian species can utilize habitats deeper in bed sediments during a portion of their life history (e.g., down to 100 cm below the sediment surface) (MacDonald et al. 2000a). The best available knowledge about the local composition of sediment-associated biota and the bioactive depth zone they occupy should supplement the generic depth assumptions above (Clarke et al. 2001) where possible. Contaminants in sediments at depths below the biologically active zone can be of concern because of their potential to move to the upper sediment strata through various mechanisms that include diffusion and being transported on groundwater flows that discharge to the surface water body. The groundwater-sediment-surface water zone is a zone of transitions in which various environmental factors can affect contaminant fate and transport.

The CBSQGs should be considered when assessing contaminated soils and sediments deposited on upper bank areas and floodplain areas that have the potential to be eroded or scoured and transported to and deposited in a nearby surface water body.

11. Other Approaches Being Used to Develop SQGs

U.S. EPA has developed national equilibrium partitioning sediment guidelines (ESGs) for a broad range of sediment types. They have finalized the methodologies for deriving ESGs for nonionic organic chemicals (2000a) and mixtures of certain metals (cadmium, copper, lead, nickel, zinc, and silver (U.S.EPA, 2000b). U.S. EPA is planning to publish final guidance (EPA, 2000c) for developing SQGs based on a combination of the equilibrium partitioning (EqP) approach, quantitative structure activity relationships, narcosis theory, and concentration addition models for mixtures of PAH found at specific sites. The EqP-based summed PAH toxicity model provides a method to address causality, account for bioavaliability, consider mixtures, and predict toxicity and ecological effects (U.S. EPA, 2000). The U.S. EPA guidance indicates that the total number of PAHs that need to be considered in SQG development is 34 (18 parent and 16 with alkylated groups). Use of fewer than 34 may greatly underestimate the total toxicological contribution of PAH mixtures. The guidance requires the use of conservative uncertainty factors to be applied when fewer than the 34 are being used to estimate site-specific toxicity of PAH mixtures.

When guidance has been published in final for the use and application of the ESGs for metals, PAH mixtures, and other nonionic organic compounds, the Water Quality Standards section plans to produce additional guidance on the use of the ESGs to be used in addition to or instead of the CBSQGs. U.S. EPA's apparent intent is not to use the ESG numeric values as stand alone criteria for application as part of a States water quality standards under Section 3 (c) of the Clean Water Act, but to use them as a screening tool in conjunction with other assessment tools such as toxicity testing in evaluating and prioritizing sites under various programs (e.g., developing Total Maximum Daily Loads (TMDLs) s and WPDES permit limitations, Superfund, RCRA).

Table 1. Recommended Sediment Quality Guideline Values For Metals and Associated Levels of Concern To Be Used In Doing Assessments of Sediment Quality.

				m	g/kg dry wt	++		
Metal	Level 1 Concern		Level 2 Concern		Level 3 Concern		Level 4 Concern	Source of SQG
	≤ TEC	TEC	> TEC ≤ MEC	MEC	> MEC ≤ PEC	PEC	> PEC	Effect-Based Concentrations
Antimony		2	⇔	13.5	⇔	25	₽	NOAA (1991) 1.
Arsenic	4	9.8	⇔	21.4	\$	33	î	CBSQG (2000a) ²
Cadmium	4	0.99	⇔	3.0	\$	5.0	î	CBSQG (2000a)
Chromium	4	43	⇔	76.5	\$	110	î	CBSQG (2000a)
Copper	Û	32	⇔	91	\$	150	Î	CBSQG (2000a)
Iron	1	20,000	\$	30,000	‡	40,000	Î	Ontario (1993) 3
Lead	1	36	⇔	83	\$	130	Ŷ	CBSQG (2000a)
Manganese	1	460	\$	780	‡	1,100	Î	Ontario (1993)
Mercury	1	0.18	\$	0.64	‡	1.1	Î	CBSQG (2000a)
Nickel		23	\$	36	\$	49	Ŷ	CBSQG (2000a)
Silver	1	1.6	*	1.9	\$	2.2	Ŷ	BC (1999) 4.
Zinc	4	120	⇔	290		460	Ŷ	CBSQG (2000a)

⁺⁺ The CBSQGs for organic compounds are expressed on a dry weight concentration at 1% TOC in sediments. However, unlike the organic compounds, the CBSQG and study site metals concentrations can be compared on a bulk chemistry basis and do not need to be adjusted to a 1% TOC basis to do the comparison. TOC does not play the same role in determining metals availability as it does in determining organic compound availability.

- 1. NOAA (1991) = Long, E.R. and L.G. Morgan. 1991. The potential for biological effects of sediment-sorbed contaminants tested in the National Status and Trends Program. NOAA Technical Memorandum NOS OMA 52. National Oceanic and Atmospheric Administration. Seattle, Washington.
- 2. CBSQG (2000a) = MacDonald, D.D., C.G. Ingersoll, and T.A. Berger. 2000a. Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. Arch. Environ. Contam. Toxicol. 39:20-31.
- 3. Ontario (1993) = Persaud, D.R., R. Jaagumagi, and A. Hayton. 1993. Guidelines for the protection and management of aquatic sediments in Ontario. Standards Development Branch. Ontario Ministry of Environment and Energy. Toronto, Canada.
- 4. MacDonald, D.D. and M. MacFarlane. 1999. (Draft). Criteria for managing contaminated sediment in British Columbia. British Columbia Ministry of Environment, Lands, and Parks. Victoria, British Columbia.

Table 2. Recommended Sediment Quality Guideline Values For Polycyclic Aromatic Hydrocarbons (PAHs) and Associated Levels of Concern To Be Used In Doing Assessments of Sediment Quality.

				ug/kg d	ry wt. at 1	% TOC **		
	Level 1		Level 2		Level 3		Level 4	Source of SQG
PAH	Concern		Concern		Concern		Concern	Effect-Based
1 701	≤ TEC	TEC	> TEC	MEC	> MEC ≤ PEC	PEC	> PEC	Concentrations
			≤ MEC	DAIL (0				
Acenapthene	<u>L</u>	ow Moleci	ular Weight	PAHS (3 o 48	r less benze	ne rings) 89		CCME (4000) 1:
•			⇔		⇔		⇒	CCME (1999) 1.
Acenaphthylene		5.9	⇔	67	⇔	128	⇒	CCME (1999)
Anthracene	⇔	57.2	⇔	451	⇔	845	⇒	CBSQG (2000a) 2.
Fluorene	4	77.4	⇔	307	\$	536	⇒	CBSQG (2000a)
Naphthalene	4	176	⇔	369	\$	561	⇒	CBSQG (2000a)
2-methylnapthalene		20.2	⇔	111	\$	201	⇒	CCME (1999)
Phenanthrene		204	⇔	687	\$	1,170	⇒	CBSQG (2000a)
	Н	igh Molecu	ılar Weight I	PAHs (4 o	r more benz			
Benz(a)anthracene		108	⇔	579	\$	1,050	₽	CBSQG (2000a)
Benzo(a)pyrene	4	150	⇔	800	\$	1,450	₽	CBSQG (2000a)
Benzo(e)pyrene		150	⇔	800	⇔	1,450	₽	Similar as above 3.
Benzo(b)fluoranthene	4	240	⇔	6,820	\$	13,400	₽	Similar as below 4.
Benzo(k)fluoranthene	4	240	⇔	6,820	\$	13,400	₽	Persaud et al. 1993 ⁵
Benzo(g,h,l)perylene	4	170	⇔	1,685	\$	3,200	₽	Persaud et al. 1993
Chrysene	4	166	⇔	728	⇔	1,290	⇒	CBSQG (2000a)
Dibenz(a,h)anthracene		33	⇔	84	⇔	135	₽	CBSQG (2000a)
Fluoranthene		423	⇔	1,327	\$	2,230	₽	CBSQG (2000a)
Indeno(1,2,3-cd)pyrene		200	⇔	1,700	\$	3,200	₽	CBSQG (2000a)
Pyrene		195	⇔	858	\$	1,520	₽	CBSQG (2000a)
			Т	otal PAHs				
Total PAHs	4	1,610	⇔	12,205	\$	22,800	₽	CBSQG (2000a)

⁺⁺ To compare the study site concentrations with the Table 2 concentrations on a common basis, divide the study site concentrations by the %TOC at the study site to yield a dry wt. normalized value at 1% TOC. If no site TOC information is available, assume a 1% TOC content.

- 1. CCME (1999) = Canadian Council of Ministers of the Environment (CCME). 1999. Canadian sediment quality guidelines for the protection of aquatic life: Summary tables. In: Canadian environmental quality guidelines. 1999. Canadian Council of Ministers of the Environment, Winnipeg.
- 2. CBSQG (2000a) = MacDonald, D.D., C.Ğ. Ingersoll, and T.A. Berger. 2000a. Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. Arch. Environ. Contam. Toxicol. 39:20-31.
- 3. There are no guideline values for Benzo(e)pyrene. "Similar as above" assumes the similarity of the chemical structure of Benzo(e)pyrene with Benzo(a)pyrene would yield similar quantitative structure activity relationships (QSARs) as it relates to toxicity, therefore the effect level concentrations that were derived for Benzo(a)pyrene would also apply to Benzo(e)pyrene.
- 4. There are no guideline values for Benzo(b)fluoranthene. "Similar as below" assumes the similarity of the chemical structure of Benzo(b)fluoranthene with Benzo(k)fluoranthene would yield similar quantitative structure activity relationships (QSARs) as it Relates to toxicity, therefore the effect level concentrations that were derived for Benzo(k)fluoranthene would also apply to Benzo(b)fluoranthene.
- 5. Ontario (1993) = Persaud, D.R., R. Jaagumagi, and A. Hayton. 1993. Guidelines for the protection and management of aquatic sediments in Ontario. Standards Development Branch. Ontario Ministry of Environment and Energy. Toronto, Canada.

Table 3. Recommended Sediment Quality Guideline Values For Polychlorinated Biphenyls (PCBs) And Chlorinated and Other Pesticides and Associated Levels of Concern To Be Used In Doing Assessments of Sediment Quality.

				ug/kg	g dry wt. at	1% TOC [↑]	·	
PCB and Pesticides	Level 1 Concern	TEC	Level 2 Concern	MEC	Level 3 Concern	PEC	Level 4 Concern	Source of SQG
	≤ TEC	IEC	> TEC ≤ MEC	IVIEC	> MEC ≤ PEC	PLC	> PEC	Effect-Based Concentrations
				PCB:	S			
Total PCBs		60	⇔	368	⇔	676	⇧	CBSQG (2000a) 1.
				Pestici	des			
Aldrin	4	2	⇔	41	⇔	80	₽	Ontario (1993) 2.
ВНС	4	3	⇔	62	⇔	120	₽	Ontario (1993)
alpha-BHC	4	6	⇔	53	⇔	100	î	Ontario (1993)
beta-BHC		5	⇔	108	⇔	210	₽	Ontario (1993)
gamma-BHC (lindane)	(3	⇔	4	⇔	5	1	CBSQG (2000a)
Chlordane	4	3.2	⇔	10.6	⇔	18	fr	CBSQG (2000a)
Dieldrin	4	1.9	⇔	32	⇔	62	î	CBSQG (2000a)
Sum DDD	4	4.9	⇔	16.5	⇔	28	fr	CBSQG (2000a)
Sum DDE		3.2	⇔	17	⇔	31	₽	CBSQG (2000a)
Sum o,p' + p,p' DDT	(4.2	⇔	33.6	⇔	63	₽	CBSQG (2000a)
Sum of DDT +DDD + DDE	.	5.3	*	289	⇔	572	Ŷ	CBSQG (2000a)
Endrin	4	2.2	⇔	104.6	⇔	207	Î	CBSQG (2000a)
Heptachlor Epoxide		2.5	⇔	9.3	⇔	16	₽	CBSQG (2000a)
Mirex		7	⇔	10.5	⇔	14	Î	BC (1999) 3.
Toxaphene		1	⇔	1.5	⇔	2	₽	BC (1999)

⁺⁺ To compare the study site concentrations with the Table 3 concentrations on a common basis, divide the study site concentrations by the %TOC at the study site to yield a dry wt. - normalized value at 1% TOC. If no site TOC information is available, assume a 1% TOC content.

^{1.} CBSQG (2000a) = MacDonald, D.D., C.G. Ingersoll, and T.A. Berger. 2000a. Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. Arch. Environ. Contam. Toxicol. 39:20-31.

^{2.} Ontario (1993) = Persaud, D.R., R. Jaagumagi, and A. Hayton. 1993. Guidelines for the protection and management of aquatic sediments in Ontario. Standards Development Branch. Ontario Ministry of Environment and Energy. Toronto, Canada.

^{3.} MacDonald, D.D. and M. MacFarlane. 1999. (Draft). Criteria for managing contaminated sediment in British Columbia. British Columbia Ministry of Environment, Lands, and Parks. Victoria, British Columbia.

Table 4. Recommended Sediment Quality Guideline Values For Assorted Contaminants and Associated Levels of Concern To Be Used In Doing Assessments of Sediment Quality.

				ug/kg	dry wt. at	1% TOC ⁺⁺		
Sediment Contaminant	Level 1 Concern ≤ TEC	TEC	Level 2 Concern > TEC ≤ MEC	MEC	Level 3 Concern > MEC ≤ PEC	PEC	Level 4 Concern > PEC	Source of SQG Effect-Based Concentrations
Benzene	1	57	⇔	83.5	\$	110	î	BC (1999) 1.
Toluene	1	890	⇔	1,345	\$	1,800	î	BC (1999)
Xylene	1	25	⇔	37.5	\$	50	î	BC (1999)
2,3,7,8-TCDD (pgTEQ/g)	4	0.85	⇔	11.2	\$	21.5	Î	Canada (2002) 2.
Pentachlorophenol	û	150	⇔	175	\$	200	₽	Janisch (1990) 3.
Tributyltin	Û	0.52	\$	1.73	\$	2.94	Î	Janisch (1994) 4.
1,2-Dichlorobenzene	Ū	23	\$		‡	23	Î	Washington (1991) ^{5.}
1,4-Dichlorebenzene	û	31	⇔	60.5	\$	90	₽	Washington (1991)
1,2,4-Trichlorobenzene	û	8	⇔	13	\$	18	Î	Washington (1991)
Dimethyl Phthalate	û	530	⇔		\$	530	⇧	Washington (1991)
Diethyl Phthalate	Ū	610	⇔	855	‡	1,100	Î	Washington (1991)
Di-N-Butyl Phthalate	Ū	2,200	⇔	9,600	‡	17,000	Î	Washington (1991)
Di-N-Octyl Phthalate	Û	580	⇔	22,790	\$	45,000	Ŷ	Washington (1991)
Dibenzofuran	Ū	150	⇔	365	‡	580	Î	Washington (1991)
Phenol	Ū	4,200	⇔	8,100	‡	12,000	Ŷ	Washington (1991)
2-Methylphenol	Û	6,700	⇔		\$	6,700	Û	Washington (1991)
2,4-Dimethyl Phenol	Û	290	⇔		\$	290	Ŷ	Washington (1991)
Benzyl Alcohol	Û	570	⇔	650	\$	730	Û	Washington (1991)
Benzoic Acid	Û	6,500	⇔		\$	6,500	î	Washington (1991)

⁺⁺ To compare the study site concentrations with the Table 4 concentrations on a common basis, divide the study site concentrations by the %TOC at the study site to yield a dry wt. - normalized value at 1% TOC. If no site TOC informatio is available, assume a 1% TOC content.

- 1. MacDonald, D.D. and M. MacFarlane. 1999. (Draft). Criteria for managing contaminated sediment in British Columbia. British Columbia Ministry of Environment, Lands, and Parks. Victoria, British Columbia.
- 2. Canadian Sediment Quality Guidelines for the Protection of Aquatic Life. Summary Table. Update 2002. Canadian Council of Ministers of the Environment.
- 3. Janisch (1990) = Memo of February 7, 1990 prepared to Maltbey of NCD entitled Sediment Quality Criteria for Pentachlorophenol related to the Semling-Menke Company Contaminated Groundwater Inflow to the Wisconsin River. Sediment guidelines for Developed for pentachlorophenol in sediment based on the water quality criteria in NR 105. Considerations made for pH of of water and organic carbon partitioning coefficient of pentachlorophenol. The pH determines the dissociated / undissociated forms of pentachlorophenol and its partitioning coefficient. The pH used to calculate the above sediment values was 7.0. The K₀c value used was 3.226 or 1,821 L/kg OC. The organic carbon content of the sediment was assumed to be 1%. The TEC and PEC values above for PCP were based on the chronic and acute water quality criteria in NR 105, respectively.
- 4. Janisch (1994) = Memo of November 14, 1994 prepared to LaValley of NWD entitled Preliminary Ecological Risk Assessment for the Contaminated Sediments Associated with the Fraser Shipyard Site, Superior, Wisconsin. Sediment guidelines for tributyltin derived based on the proposed water quality criteria for tributyltin at the time (EPA, 1988). The organic carbon partitioning coefficient used was 1,970 L/kg OC and an assumed organic carbon content of 1% in sediment. The TEC and PEC values above for tributyltin were based on the chronic and acute water quality values as proposed by EPA, respectively.
- 5. Washington (1991) = Sediment Management Standards, Chapter 173-204 WAC, Washington State Department of Ecology. April 1991. The Standards were developed using the Apparent Effects Threshold Approach. The TEC and PEC values above for the compounds are based on no effect and minimal effect standards, respectively, from the Washington Standards and are intended to apply to Puget Sound, an estuarine habitat. The values were calculated based on an assumed TOC content in sediment of 1%.

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Appendix A

Recommended Procedure for Calculating Mean Probable Effect Quotients (Mean PEC Quotients) for Mixtures of Chemicals found at Contaminated Sediment Sites and Their Reliability of Predicting the Presence or Absence of Toxicity (Adopted from Ingersoll *et al.* 2000, 2001).

- Step 1. Based on existing databases, the reliability to predict toxicity is greatest for the organic compound groups of total PAHs and total PCBs and the metals arsenic, cadmium, chromium, copper, lead, nickel, and zinc. Inclusion of other compounds or metals that have a PEC value, where there is insufficient data available to evaluate its predictive reliability (e.g., mercury, dieldrin, DDD, DDT, endrin, and lindane) into the overall PEC-Q calculation may result in an overall PEC-Q value with lower predictive ability.
- Step 2. Calculate the individual PEC Quotients (PEC-Qs) for chemicals with reliable PECs within each of the chemical classes. Since the PECs for PAH and PCB chemical classes are based on total concentrations, individual PEC-Qs for individual compounds in these classes do not need to be calculated.

Individual Chemical PEC-Q = Chemical concentration in Study Site Sediments (in dry wt.)

PEC SQG Concentration for Chemical (in dry wt.)

For the nonpolar organic compounds (total PCBs and total PAHs), the PEC SQG is expressed on a dry weight basis normalized to 1% organic carbon. The concentration for these groups of nonpolar compounds in the study site sediments also needs to be expressed on this same basis. To do this, divide the concentration in the study site sediments by the percent TOC in the sediments expressed as a whole number (e.g., 7,300 ug/kg PCB at 5% TOC is $7,300 \div 5 = 1,460 \text{ mg/kg}$ dry weight normalized to 1% TOC).

Step 3. In the case of metals, a mean PEC-Q_{metals} for the metals involved needs to be calculated based on summing the PEC-Q for the individual metals and dividing by the number of metals.

Mean PEC-Q_{metals} =
$$\underline{\Sigma \text{ individual metal PEC-Qs}}$$

Number of metals for which individual PEC-Qs calculated

Step 4. Calculate the overall mean PEC-Q for the three main classes of chemicals.

$$Mean PEC-Q_{overall} = \underbrace{(mean PEC-Q_{metals} + PEC-Q_{total PAHs} + PEC-Q_{total PCBs})}_{n}$$

Where n = number of classes of chemicals for which sediment chemistry available (e.g., in this case, there are three classes – metals, PAHs and PCBs. In other cases, metals and PAHs may be the only chemicals of concern at a site and therefore PEC-Qs may only be calculated for these two groups and therefore n = 2.

Appendix A (continued)

The database used by Ingersoll et al. (2001) to determine the ability of the PEC-Qs to predict toxicity is based on testing freshwater sediments from a number of sites using 10- to 42-day toxicity tests with the amphipod *Hyalella azteca* or the 10- to 14-day toxicity tests with the midges *Chironomus tentans* or *C. riparius*. Toxicity of samples was determined as a significant reduction in survival or growth of the test organisms relative to a control or reference sediment. A relative idea of the predictive ability of the overall mean PEC-Qs and individual PEC-Qs for each group of chemicals is shown in the table below from Ingersoll et al. (2001). Mean PEC quotients were calculated to provide an overall measure of chemical contamination and to support an evaluation of the combined effects of multiple contaminants in sediments.

Test Species and Test Duration	Incidence o	ed versus no	Total Number of Samples			
	< 0.1	0.1 to < 0.5	e of Mean PEC Q 0.5 to < 1.0	1.0 to < 5.0	> 5.0	Campies
Hyalella azteca 10- to 14-day tests						
Mean Overall PEC-Q 1.	19 (79)	26 (89)	38 (34)	49 (35)	86 (29)	266
Q _{metals} ^{2.}	23 (40)	24 (139)	33 (45)	81 (31)	100 (11)	266
PEC-Q _{total PAHs} 3.	25 (123)	33 (76)	35 (20)	49 (33)	100 (14)	266
PEC-Q _{tota} l _{PCBs} 4.	20 (98)	25 (61)	47 (43)	47 (34)	73 (30)	266
Hyalella azteca 28- to 42-day tests					> 1.0	
Mean Overall PEC-Q	4 (45)	6 (18)	50 (18)	NC 5.	100 (28)	109
PEC-Q _{metals}	5 (40)	25 (24)	60 (33)	NC	100 (12)	109
PEC-Q _{total PAHs}	8 (57)	64 (37)	55 (9)	NC	100 (6)	109
PEC-Q _{total PCBs}	4 (26)	6 (35)	17 (12)	NC	97 (36)	109
Chironomus spp. 10- to 14-day tests					> 5.0	
Mean Overall PEC-Q	29 (21)	35 (78)	35 (26)	50 (34)	78 (18)	177
PEC-Q _{metals}	8 (12)	43 (107)	22 (36)	75 (12)	90 (10)	177
PEC-Q _{total PAHs}	26 (64)	33 (73)	77 (13)	85 (20)	71 (7)	177
PEC-Q _{total PCBs}	48 (58)	23 (31)	34 (32)	35 (34)	68 (22)	177

^{1.} Mean Overall PEC-Q = Based on samples where average metal quotient, total PAH quotient, and PCB quotient summed and divided by 3.

In samples where the metals, total PAHs, and total PCBs were all measured, each of the three PEC-Qs were evaluated individually to determine their predictive ability, yielding the individual PEC-Q values below.

- 2. PEC-Q_{metals} = Average PEC quotient for the number of metals involved calculated.
- 3. PEC-Q_{total PAHs} = Based on the samples where individual PAHs measured in samples which were summed to yield a total PAHs value.
- 4. PEC-Q_{total PCBs} = Based on samples where total PCBs measured in samples.
- 5. NC = Not calculated.

Appendix A (continued)

Observations from Ingersoll et al. (2001):

- There was an overall increase in the incidence of toxicity with an increase in the mean quotients in toxicity tests involving all three test organisms.
- A consistent increase in the toxicity in all three tests occurred at a mean quotient of > 0.5. However, the
 overall incidence of toxicity was greater in the *Hyalella azteca* 28-day test compared to shorter term tests.
 The longer term tests, in which survival and growth are measured, tend to be more sensitive than the
 shorter term tests, with the acute to chronic ratios on the order of six indicated for *Hyalella azteca*.
- The use of chronic laboratory toxicity tests better identified chemical contamination in sediments compared
 to many of the commonly used measures of benthic invertebrate community structure. The use of longerterm toxicity tests in combination with SQGs may provide a more sensitive and protective measure of
 potential toxic effects of sediment contamination on benthic communities compared to use of the 10-day
 toxicity tests.
- There appears to be different patterns of toxicity when the PEC-Qs for the chemical classes are used alone
 or combined. The different patterns in toxicity may be the result of unique chemical signals associated with
 individual contaminants in samples. While the combined mean PEC quotient value from the chemical
 classes can be used to classify samples as toxic or nontoxic, individual PEC quotients of each chemical
 class might be useful in helping identify substances that may be causing or substantially contributing to the
 observed toxicity.
- The results of the evaluation indicate that the consensus-based PECs can be used to reliably predict toxicity of sediments on both a regional and national basis.

Example Calculation

The analytical results for a sediment sample and the steps to derive a mean overall PEC-Q for all the contaminants are as follows:

				mg/kg	dry wt.						
	Sample Bulk Sediment Concentrations										
			Organics								
Arsenic	Cadmium	Copper	Total PAHs	Total PCBs	TOC						
75	9	170	90	270	65	320	108	9.2	2.5%		
water and its normalized c to compare d for the purpo	Since TOC does not play a major role in the partitioning of metals from the sediments to the sediment pore water and its subsequent bioavailability, it is not necessary to convert metals concentrations to a dry weight normalized concentration at 1% TOC. Use the bulk sediment concentration as reported on the lab sheets to compare directly with the PEC SQGs. Normalization of metals concentrations to the fine fraction is done for the purposes of comparing the study site metal concentrations with the reference site concentrations on a common basis and is not related to the SQGs.										
75	9	170	90	270	65	320	43.2	3.68			
	De	termine the F	EC concentrat	ions for each	contaminant (fro	m Tables 1, 2	2, and 3 above	e).			
33	5	150	110	130	49	460	22.8	0.68			
		(Calculate the F	PEC-Q for ea	ch contaminant. S	step 2 above.					
2.27	1.8	1.13	0.82	2.08	1.33	0.70	1.89	5.41			
	Calcu	ılate a mean l	PEC-Q for the	metals. Step	3 above.						
			1.45				1.89	5.41			
	Calculate an o	overall mean l	PEC-Q value fi	om the 3 che	emical classes (me	etals, PAHs,	and PCBs). S	Step 4 above.			
				Mean PE	C-Q = 2.92						

Compare the 2.92 value with the ranges of PEC-Q values in the table above. For the shorter-term toxicity tests with *Hyalella azteca* and *Chironomus spp.*, a value of 2.92 is in a range where 50% of the samples were toxic. For the longer-term tests with *H. azteca*, all of the samples were toxic at the PEC-Q value of 2.92. It appears based on these results, *H. azteca* or benthic organisms of similar sensitivity in the field populations may be significantly impacted by the concentrations of contaminants present. If these results represented an actual site, further assessments of the site is warranted.

Observations From MacDonald et al. (2000)

MacDonald *et al.* (2000) also looked at the predictive ability of the CBSQGs. To examine the relationships between the degree of chemical contamination and probability of observing toxicity in freshwater sediments, the incidence of toxicity within various ranges of mean PEC quotients was calculated from an existing database. The data were plotted in a graph (Table 1, MacDonald *et al.* 2000). The interpolated data from this graph is in the table below. MacDonald *et al.* found that subsequent curve-fitting indicated that the mean PEC-quotient is highly correlated with incidence of toxicity ($r^2 = 0.98$), with the relationship being an exponential function. The resulting equation (Y = 101.48 (1-0.36^X) can be used to estimate the probability of observing sediment toxicity at any mean PEC quotient.

Relationship between Mean PEC Quotient and Incidence of Toxicity in Freshwater Sediments						
(Derived and Interpolated from MacDonald et al. 2000a)						
Mean PEC Quotient Average Incidence of Toxicity (%)						
0	0					
0.25	20					
0.50	40					
0.75	54					
1.00	64					
1.25	70					
1.50	77					
1.75	84					
2.00	87					
2.25	90					
2.50	92					
2.75	95					
3.00	96					
3.25	98					
3.50	99					
3.75	99.5					
≥ 4.00	100					

Utilizing the mean PEC-Quotient of 2.92 calculated in the example above yields a predicted average incidence of toxicity of approximately 95% based on the table immediately above. The chances are likely that if a sampled site yields a mean PEC-Q of 2.92, significant toxicity to infaunal species will be present.

Appendix B

Recommended Procedure for Calculating the Maximum Probable Background Concentration (MPBC) For a Metal or Organic Compound at Reference or Background Sites

Calculating the 95% upper confidence limit (UCL) of the mean of a data set of background concentrations for a parameter. Use of the UCL as the maximum probable background concentration (MPBC) for comparison purposes with the study site concentrations (Adapted from EPA, 1992b).

Statistical confidence limits are a tool for addressing uncertainties of a distribution average. The 95% UCL of the arithmetic mean concentration is used as the average concentration because it is not possible to know the true mean. The 95% UCL therefore accounts for uncertainties due to limited sampling data. As sample numbers increase, uncertainties decrease as the UCL moves closer to the true mean. Sampling data sets with fewer than 10 samples may provide a poor estimate of the mean concentration (i.e., there is a large difference between the sample mean and the 95% UCL). Data sets with 10 to 20 samples may provide a somewhat better estimate of the mean (i.e., the 95% UCL is close to the sample mean). In general, the UCL approaches the true mean as more samples are included in the calculation.

Transformation of the Data

The data set for the background concentrations should be looked at to determine if the data is lognormally or normally distributed. A statistical test should be used to identify the best distributional assumption for the data set. The W-test (Gilbert, 1987) is one statistical method that can be used to determine if a data set is consistent with a normal or lognormal distribution. In all cases, it is useful to plot the data to better understand the parameter distribution in the background or reference site area.

Assuming the data set for the background concentrations is normally distributed, the 95% UCL is calculated by the following four steps:

- 1) Calculate the arithmetic mean of the untransformed data.
- 2) Calculate the standard deviation of the untransformed data.
- 3) Determine the one-tailed *t*-statistic (see a statistical text for the Student *t Distribution* table).
- 4) Calculate the UCL using the following equation:

UCL = x + t (s / square root of n)

Where:

UCL = Upper Confidence Level of the Mean to be used as the maximum probable background concentration (MPBC).

- x = Mean of the data
- s = Standard deviation of the data
- t = Student-t statistic from statistical textbook
- n = number of samples

APPENDIX B (continued)

Example Calculation

10 samples were taken at a background site for mercury that had comparable hydrologic and sediment characteristics as the site under study but was not influenced by the sources of mercury contamination at the study site. The background sample concentrations for mercury were: 15, 30, 33, 55, 62, 83, 97, 104, 125, and 155 ug/kg.

Following the 4 steps above –

- 1) Mean mercury concentration 75.9 ug/kg
- 2) Standard deviation 45.02
- 3) Student t-statistic value for one-tail test. n = 10 samples. Degrees of freedom 10 1 = 9. t-distribution 1.833
- 4) UCL = x + t (s / square root of n) UCL = 75.9 + 1.833 (45.02 / square root of 10) UCL = 75.9 + 1.833 (45.02 / 3.16) UCL = 75.9 + 1.833 (14.25) UCL = 75.9 + 26.12 UCL = 102.02 ug/kg

The UCL value for mercury of 102.02 ug/kg becomes the maximum probable background concentration (MPBC) that will be used to compare the study site concentrations against. Concentrations of mercury in study site sediment samples that are greater than the 102.02 ug/kg value can be considered to be influenced by the sources of mercury other natural or ubiquitous (e.g., atmospheric depositions) sources. As discussed above in the main body of this document, the percent fine fractions need to be looked at in the sediment samples under comparison. If the relative contribution of fines are the same in the samples from the background site and the study site, then no adjustments need to be made. If the percent fines are significantly different between the samples and the sites, then considerations for normalization of the mercury concentrations to the fine content should be looked at in order to do relevant site-to-site comparisons of metal concentrations.

The CBSQG TEC value for mercury is 180 ug/kg (Table 1 above). The MPBC for mercury in this example at 102.02 ug/kg is less than the MPBC value. An interpretation of this relationship is that benthic macroinvertebrates are possibly tolerant of mercury concentrations that are somewhat greater than background concentrations. This relationship may come into play if a decision is made to use the greater of the MPBC or the TEC value to drive the cleanup of a site.

An example of what fewer background samples would mean to the resulting MPBC value can be seen by the following example using only 4 of the sample results for mercury – 30. 62, 104, and 155 ug/kg.

- 1) Mean mercury concentration 87.8ug/kg
- 2) Standard deviation 54.11
- 3) Student t-statistic value for one-tail test for n = 4 samples. Degrees of freedom 4 1 = 3 t-distribution -2.353

UCL = x + t (s / square root of n)

UCL = 87.8 + 2.353 (54.11 / square root of 4)

UCL = 87.8 + 2.353 (54.11 / 2)

UCL = 87.8 + 2.353 (27.06)

UCL = 87.8 + 63.7

UCL = 151.5 ug/kg

APPENDIX C

Notes on Dioxins and Furans

- Polychlorinated dibenzo-p-dioxins and dibenzofurans are ubiquitous contaminants, primarily from combustion sources. Background concentrations are normally in the range 0.15 - 2.5 pg TCDD-EQ/g Sediment.
- There are concerns with the other 2,3,7,8-substituted congeners beside 2,3,7,8-TCDD and TCDF. There is a need to request that all 17 2,3,7,8 substituted congeners be analyzed for. Analytical costs are high. To do an adequate environmental assessment, detection levels for 2,3,7,8-TCDD need to be at the single digit pg/g level.
- Dioxins and furans are not produced commercially but are unintended by-products from various chemical manufacturing and other sources.
- Dioxins and furans are found in discharges from wood treatment facilities that use pentachlorophenol, kraft pulp mills, and chemical manufacturing plants that produced pentachlorophenol, trichlorophenol, and the pesticides 2,4-D and 2,4,5-T. Also, if a water body has a history of aquatic applications of the herbicide Silvex, residual dioxins and furans may be present
- For some perspective, the department's landspreading program for paper mill sludges sets limits for spreading based on land uses Silviculture 10 pg/g; Agriculture 1.2 pg/g; Grazing 0.5 pg/g.
- Examples of high levels of dioxins/furans at Wisconsin sediment sites include Crawford Creek discharge from wood treatment facility that used pentachlorophenol 5,500 pg TCDD-EQ/g; Military Creek-discharge from wood treatment facility that used pentachlorophenol 2,500 pgTCDD-EQ/g; Fox River paper mill discharges 21 441 pg TCDD-EQ / g; and Wisconsin River paper mill discharges 31 78 pg TCDD-EQ / g.
- The recommendation is that dioxin and furan analysis only be done where there is a demonstrated need given the identification of possible historical sources at a site.
- The different 2,3,7,8 substituted dioxins and furans have toxic equivalency factors (TEF) assigned to them relative to their toxicity compared to 2,3,7,8-TCDD. The table below provides a method to calculate the summed TCDD equivalent concentration for all the substituted forms in a sample.

2,3,7,8 - Substituted Dioxin and Furan Congeners

Worksheet For Calculating 2,3,7,8-TCDD Equivalent Concentrations	Sediment Concentration pg/g (ppt) dry weight	Toxic Equivalency Factors (TEF) (Equivalency to 2,3,7,8-TCDD)	pg/g x TEF = Toxic Equivalency to 2,3,7,8-TCDD Or TCDD-EQ
Dioxins			
2,3,7,8-TetraCDD		1.0	
1,2,3,7,8-PentaCDD		0.5	
1,2,3,4,7,8-HexaCDD		0.1	
1,2,3,6,7,8-HexaCDD		0.1	
1,2,3,7,8,9-HexaCDD		0.1	
1,2,3,4,6,7,8-HeptaCDD		0.01	
OctaCDD		0.001	
Furans			
2,3,7,8-TetraCDF		0.1	
2,3,4,7,8-PentaCDF		0.5	
1,2,3,7,8-PentaCDF		0.05	
1,2,3,4,7,8-HexaCDF		0.1	
1,2,3,6,7,8-HexaCDF		0.1	
2,3,4,6,7,8-HexaCDF		0.1	
1,2,3,7,8,9-HexaCDF		0.1	
1,2,3,4,6,7,8-HeptaCDF		0.01	
1,2,3,4,7,8,9-HeptaCDF		0.01	
OctaCDF		0.001	
Sum of TCDD-EQ of Individual S (pg TCDD-			

APPENDIX D

Dry Weight Sediment Concer TOC for Comparison with CE S		d Grain S	Size Nori			
Sample Site:		Example Calculations (Request a copy of Excel Spreadsheet)			heet)	
Sample Description:						
Date:						
ug/g = ppm = mg/kg						
ng/g = ppb = ug/kg						
TOC repo	rted as m	g/kg ÷ 10	,000 = %	TOC		
	Bulk Ch					
Parameter	Concen- tration	Units	% TOC in Sample			
TOC	25,000	mg/kg	2.	<u>5</u> %		
Dry Wt. Concentration ÷ TOC ex	xpressed a		oncentra	tion Norm	nalized to 1	% TOC
PAHs	Dry W		Nor	malized	to 1% TO	C for
FAIIS	Concen	tration	Compa	rison Wit	th CBSQG	Values
Acenapthene	3.2	ug/kg	1.3	ug/kg @	1% TOC	
Acenaphthylene	5.9	ug/kg	2.4	ug/kg @	1% TOC	
Anthracene	57.2	ug/kg	22.9	ug/kg @	1% TOC	
Fluorene	77.4	ug/kg	30.9	ug/kg @	1% TOC	
Napthalene	176	ug/kg	70.4	ug/kg @	1% TOC	
2-Methylnapthalene	20.2	ug/kg	8.1		1% TOC	
Phenanthrene	204	ug/kg	81.6	ug/kg @	1% TOC	
Benzo(a)anthracene	108	ug/kg	43.2	ug/kg @	1% TOC	
Benzo(a)pyrene	150	ug/kg	60	ug/kg @	1% TOC	
Benzo(e)pyrene	150	ug/kg	60	ug/kg @	1% TOC	
Benzo(b)fluoranthene	240	ug/kg	96	ug/kg @	1% TOC	
Benzo(k)fluoranthene	240	ug/kg	96		1% TOC	
Benzo(g,h,i)perylene	170	ug/kg	68		1% TOC	
Chrysene	166	ug/kg	66.4		1% TOC	
Dibenz(a,h)anthracene	33	ug/kg	13.2		1% TOC	
Fluoranthene	423	ug/kg	169.2		1% TOC	
Indeno(1,2,3-c,d)pyrene	200	ug/kg	80		1% TOC	
Pyrene	195	ug/kg	78		1% TOC	
,						
Total PAHs (sum of 18 PAHs listed above)	2618.9	ug/kg	1,047.6	ug/kg @	1% TOC	

	Pesticides	Concen- tration	Units	Comp	ormalized to 1% TOC for parison With CBSQG Values	
	(total)	60	ug/kg	21	ug/kg @ 1% TOC	
	drin	2	ug/kg	0.8	ug/kg @ 1% TOC	
	HC	3	ug/kg	1.2	ug/kg @ 1% TOC	
	BHC	6	ug/kg	2.4	ug/kg @ 1% TOC	
B-BHC		5	ug/kg	2	ug/kg @ 1% TOC	
Y-BHC	(lindane)	3	ug/kg	1.2	ug/kg @ 1% TOC	
Chlor	rdane	3.2	ug/kg	1.3	ug/kg @ 1% TOC	
Die	ldrin	1.9	ug/kg	0.8 ug/kg @ 1% TOC		
Sum p	p DDD	4.9	ug/kg	1.9 ug/kg @ 1% TOC		
	p DDE	3.2	ug/kg	1.3 ug/kg @ 1% TOC		
Sum op -	+ pp DDT	4.2	ug/kg	1.7 ug/kg @ 1% TOC		
Sum of DDT a	nd metabolites	5.3	ug/kg	2.1	ug/kg @ 1% TOC	
Endrin		3	ug/kg	1.2	ug/kg @ 1% TOC	
Heptachlor Epoxide		2.5	ug/kg	1.0	ug/kg @ 1% TOC	
Mirex		7	ug/kg	2.8	ug/kg @ 1% TOC	
Toxaphene		1	ug/kg	0.4	ug/kg @ 1% TOC	
Metals						
	% sand	50	%			
Particle Size	% silt		%		Fine Fraction	
	% clay	25	%	Silt + Clay = 50% or 0.50		
Dr. Mt. Consentration: Fines companded to decimal function - Newscalled to Fine						

Dry Wt. Concentration ÷ Fines expressed as decimal fraction = Normalized to Fine Concentration

Concontitution					
Metals	Dry Weight Concentration (Compare with CBSQGs		Normalized to Fine Concentration for Site-to-site Comparisons(Not for		
			Comparison with CBSQGs)		
Antimony	2	mg/kg	4	mg/kg fines	
Arsenic	9.8	mg/kg	19.6	mg/kg fines	
Cadmium	0.99	mg/kg	1.98	mg/kg fines	
Chromium	43	mg/kg	86	mg/kg fines	
Copper	32	mg/kg	64	mg/kg fines	
Iron	20,000	mg/kg	40,000	mg/kg fines	
Lead	36	mg/kg	72	mg/kg fines	
Manganese	460	mg/kg	920	mg/kg fines	
Mercury	0.18	mg/kg	0.36	mg/kg fines	
Nickel	23	mg/kg	46	mg/kg fines	
Silver	1.6	mg/kg	3.2	mg/kg fines	
Zinc	120	mg/kg	240	mg/kg fines	

Appendix E

Identification of Contamination that Leads to Adverse Effects

Contamination of a chemical nature (i.e., a contaminant) is a substance or substances (either organic or inorganic) that are present in environmental media such as sediments or surface waters that are found above levels that would normally occur. What is normal or background for metals or nutrients (e.g., nitrogen, phosphorus) would be those metals and nutrients at levels that originate from the natural soil types and the geochemical components of the watershed. What is normal for natural organic compounds would generally be those compounds that originate from natural watershed-source vegetative or animal matter that are deposited on the bottoms of lakes, streams, and wetlands. Organic chemicals manufactured by humans and released to the environment by various mechanisms generally do not have counterparts found in nature and therefore any levels found in environmental media would be considered potential contamination. Many manufactured organic compounds may be found ubiquitously at low levels in sediments especially in urban areas.

Environmental concerns arise when the level of contamination (concentration of contaminants) in surface waters and sediments leads to observed and measurable effects to biological receptors, such as 1) chronic and/or acute toxicity (the contaminant becomes a toxicant) to aquatic receptors (for example directly to aquatic life such as bottom inhabiting macroinvertebrates), and/or 2) concerns about humans and wildlife that are upper food chain organisms who may become exposed to harmful levels of contaminants principally through consumption of aquatic organisms that have bioaccumulated the contaminants. For the toxicity to aquatic organisms to be realized and/or unacceptable levels of bioaccumulation to occur, the aquatic organism has to (a) be exposed to the potential toxicant in its habitat, (b) the potential toxicant has to be in a form available for uptake, and (c) the uptake or dose of the contaminant has to be at a level that causes toxicity to the particular exposed receptor or results in levels of bioaccumulation that may pose risks to humans and/or wildlife who consume the exposed receptor as food.

Elevated levels of nutrients can lead to eutrophication of water bodies and production and deposition plant materials in sediments that deplete oxygen levels in the water body when they decompose. Addition and decomposition of natural organic matter and anthropogenic-added organic matter in sediments can lead to production of hydrogen sulfide and ammonia levels that may be detrimental to benthic organisms.